A Structural Probe of the Doped Holes in the Cuprates

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Fifteen years after its discovery the only thing known for certain about high temperature superconductors is that they cannot be described by an independent electron or even weakly-interacting Fermi liquid theory. This has led theorists to propose a variety of collective phases to explain their behavior, such as the "stripe" phase (Zaanen, 1989; Löw, 1994), the d-density wave phase (Chakraborty, 2001), the staggered flux phase (Marston, 1989; Wen, 1996), the "Varma" phase (Varma, 1997), anyons (Zou, 1992), visons (Senthil, 2000), and so on. A recurring theme among such theories is the tendency for interactions to introduce *new length scales* into a system. In a noninteracting electron gas the only length scales are the lattice parameter and the inverse Fermi momentum, $1/k_F$. In a true collective state, other length scales may enter.

There is now evidence from scanning tunneling microscopy (STM) that the density of states in the cuprates is *spatially inhomogeneous*, with correlation length $\xi \sim 14 - 30$ Å (Pan, 2000; Howald, 2001). It is not known if this is intrinsic to superconductivity or an artifact of defects or surface reconstruction. But it highlights the need for a real, momentum-resolved scattering probe of the carriers *as they reside in the ground state* to determine what length scales participate in superconductivity.

In the past no such probe has existed, for the simple reason that the doped holes make up a very small fraction of the total charge density in the cuprates - about 1/500 in optimally doped $La_{2-x}Sr_xCuO_4$. So traditional x-ray and electron scattering, which weight all charges equally, are insensitive to weak carrier modulations that might arise from interactions. Furthermore, in cases where unusual length scales have been seen (Tranquada, 1998) one cannot determine if they are truly carrier modulations or just distortions in the atomic lattice.

In this highlight we show that anomalous *soft* x-ray scattering in the prepeak region of the Oxygen *K* edge (535 eV) of the cuprates can selectively magnify the amplitude for scattering from doped holes by a factor of 82. This greatly enhances sensitivity to carrier modulations, and also provides a means to discriminate such modulations from distortions in the lattice. This technique is reminiscent of resonant magnetic x-ray scattering, where the circular dichroism induced in an atom is used to enhance sensitivity to the local magnetic moment. The spatial resolution of this technique is modest ($\lambda/2 \sim 11$ Å), however it is well matched to many of the phases mentioned above. This is, by all standards, the first structural probe of the superconducting ground state.

For these measurements we constructed a ten axis, vacuum diffractometer for scattering of soft x-rays. The system consists of a 6 degree-of-freedom sample stage, a two-axis detector arm which moves in a horizontal geometry (P polarization), and a channeltron detector stage with multilayer analyzer for background rejection, all actuated with vacuum-compatible stepper motors. The sample environment is controlled with a He flow cryostat and a 5 T superconducting magnet. The instrument sits inside a 1.2 x 1.2 x 0.8 m vacuum chamber, pumped with turbo- and titanium sublimation pumps, and moves reproducibly with a base pressure of 2×10^{-10} mbar. It currently operates on the undulator line X1b at the National Synchrotron Light Source.

The current measurements were made on epitaxial thin films of oxygen-doped $La_2CuO_{4+\delta}$, synthesized with the advanced Combinatorial Molecular Beam Epitaxy system at Oxxel (Bozovic, 2001). Film thicknesses were 20, 30, or 40 unit cells (i.e., 26, 39, or 52 nm, respectively) deposited on $SrTiO_3$ or $LaSrAlO_4$ substrates with (001) surface orientation. The films were characterized by Reflection High-Energy Electron Diffraction (RHEED), atomic-force microscopy (AFM), conventional X-ray diffraction (XRD), and transport measurements. They were essentially atomically smooth, with RMS roughness of 0.2-0.6 nm over an area of (1 μm)^2. XRD typically showed rocking curves of 0.1º with no unwanted phases, as well as finite thickness oscillations in low-angle reflectance measurements. The latter indicates that the crystalline coherence length is equal to the film thickness, and that the two film surfaces are parallel on the scale of the x-ray wavelength (0.15 nm). To make the films superconducting they were post-annealed in ozone at 150-200 ºC for 10-30 minutes and then quenched rapidly to room temperature to trap oxygen. The high quality of these films was invaluable for cleanly demonstrating resonance effects.

The soft x-ray optics of the cuprates are highly sensitive to the local hole density, and it is this property that provides carrier enhancement in diffraction. Two features which are universal to High T_c materials are the Cu*L* (933 eV) and O*K* (534 eV) edges, which correspond to removal of an electron from Cu2*p* and O1*s* inner shells, respectively. In x-ray absorption spectra (XAS) these features appear as edge jumps, with fine structure near threshold determined by band structure and atomic multiplet effects. In the insulating (undoped) cuprates the O*K* edge exhibits a "prepeak" feature just below threshold (538 eV) which is an intersite O1*s* → Cu3*d* transition (Chen, 1991). This feature is almost a third the size of the full edge jump because of strong mixing between valence O2*p* and Cu3*d* states. The Cu*L* edge comprises two enormous peaks (Figure 1, blue line), which are on-site, dipole-allowed 2p → 3d transitions where the 2*p* hole has j = 1/2 or 3/2. Because valence states are highly polarized in the CuO_2 plane both the Oxygen prepeak and the Cu*L* features are highly polarization dependent, and are observable in XAS only when **E**||ab (Chen, 1992).

When the system is doped something unusual happens. Because the undoped cuprates are charge-transfer insulators (Zaanen, 1985) added holes go into O2*p* states and a *second* prepeak, which we will call the "mobile carrier peak", appears at 535 eV (Figure 1, red circles). Its oscillator strength builds rapidly with hole concentration as states near the Fermi level are vacated, and also because doping causes spectral weight to be *transferred to 535 eV from the feature at 538 eV*. A transfer of spectral weight with doping is the classic signature of a correlated electron system (Eskes, 1991) and it makes the optical response at 535 eV extremely sensitive to the local hole density.

This sensitivity can be exploited in diffraction by realizing that the amplitude for elastic light scattering from a material is proportional to the dielectric susceptibility (Jackson, 1999), which is directly related to absorption data. XAS is quantified by an absorption coefficient, $\mu(\omega)$ ($[\mu]$ = cm^{-1}) which is related to the optical constants of the material by $\mu = 2\,k\,\mathrm{Im}[n(\omega)]$, where $k = 2\pi/\lambda$ and $n(\omega)$ is the refractive index. To determine the susceptibility one need only calculate $\mathrm{Im}[n(\omega)]$ from μ, Kramers-Krönig transform to get $\mathrm{Re}[n(\omega)]$, and apply the relation $\chi(\omega) = (\sqrt{n(\omega)} - 1)$ (MKS units). A quantitative determination of $\chi(\omega)$ in this manner should show how large the influence of the mobile carrier peak on scattering really is.

In many cases, including the present one, $\mu(\omega)$ cannot be measured directly but must be inferred from fluorescence yield (FY) measurements. From FY μ can

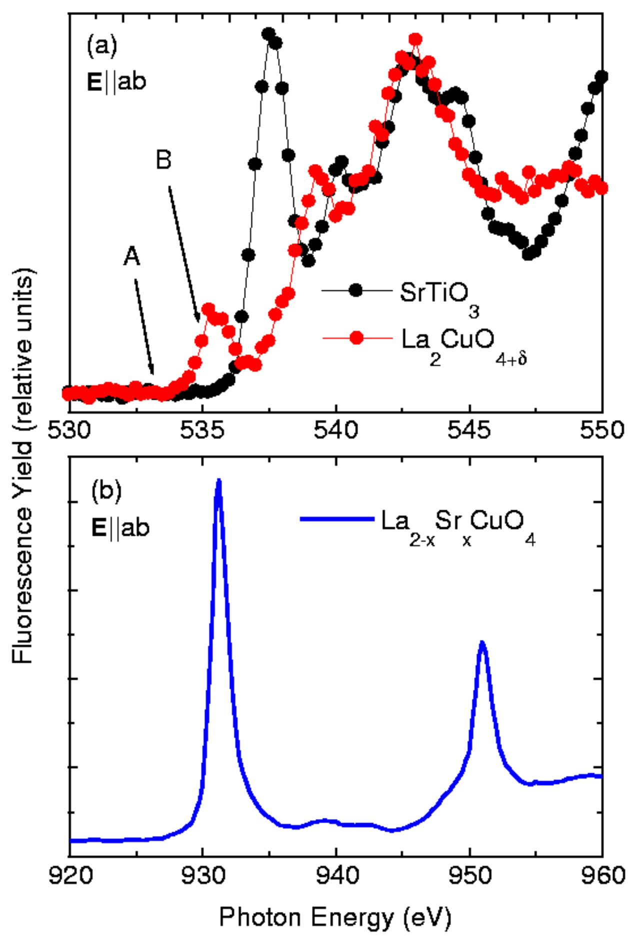

***Figure 1.** X-ray absorption spectra of optimally doped $La_{2-x}Sr_xCuO_{4+\delta}$ and $SrTiO_3$, taken in Fluorescence Yield mode. (a) Our data in the vicinity of the Oxygen* K *edge, showing the mobile carrier peak set off from other features, and (b) around the Cu*L* edge, reproduced by permission from Chen (1992). All spectra are for **E**||ab.*

be determined only within one additive and one multiplicative constant. It is still possible to put things on quantitative footing by appealing to the tabulated atomic scattering factors, which give a reliable number for $n(\omega)$ for any material far from threshold. If FY data are taken over a broad energy range the scale can be determined by matching experimental and tabulated data far from the edge. This yields a quantitative measure of $\mu(\omega)$ over the full range, which can be used to determine χ. We have followed this procedure on the FY data in Figure 1 to calculate the susceptibility for optimally doped $La_{2-x}Sr_xCuO_{4+\delta}$ around the O*K* and Cu*L* edges. The results are shown in Figure 2.

The function $\chi(\omega)$ in Figure 2 is, by assumption, the $k = 0$ (average) value. Its influence on diffraction comes from the fact that at 535 eV $\chi(\omega)$ will be *modulated in real space* if the carrier density is inhomogeneous. In depleted regions the mobile carrier peak may be nonexistent and χ will have its pre-resonance value. In regions of high carrier density, on the other hand, the peak will be enhanced. To quantify the difference we define a *contrast function*, $\Delta = |(\chi_{doped}-\chi_{insulating})/\chi_{insulating}|$, which is an indicator of the difference in scattering amplitude between regions of high and low carrier density. Far from any resonance this quantity is given by the difference in electron density, or $\Delta \sim 1/500$. According to the data of Figure 2, at the mobile carrier peak Δ jumps to 0.16. In other words, at 535 eV the scattering amplitude from doped holes is resonantly enhanced by a factor of 0.16 x 500 = 82. This will greatly enhance experimental sensitivity to variations in hole density. Furthermore, this enhancement can be switched on and off to discriminate between scattering from carriers vs. structural distortions, even when both exist.

It is worth mentioning that the effect of the 2p $\rightarrow$ 3d peaks at the Cu*L* threshold, when quantified in the same way, is truly enormous. Defining χ_{CuL} as the susceptibility at 933 eV and χ_{offres} as the value 20 eV below the edge, the quantity $|(\chi_{CuL}-\chi_{offres})/\chi_{offres}| = 0.78$. This means that the susceptibility jumps 78% at the Cu*L* edge, or in other words at 933 eV the Cu atoms scatter with an effective atomic number of Z = 165. In terms of anomalous scattering factors this gives $\Delta f_{Cu}' = 136$. Since this feature is not very doping dependent it does not aid our study of the superconducting carriers. But an anomalous scattering factor of this size is without precedent in x-ray scattering and demonstrates how large spectroscopy effects in the soft x-ray regime can be.

The carrier enhancement we have described can be demonstrated experimentally in energy- and angle-dependent reflectivity measurements of our oxygen doped films, shown in Figure 3. This film is 23.2 nm thick, grown under tensile strain on (001) $SrTiO_3$ (T_c = 39K). In the reflectivity of a film one might expect to see interference fringes with angular maxima occurring at $2d\sin(\theta) = n\lambda$. However at ω = 533 eV, labeled "A" in Fig. 1a, fringes are hardly visible (Figure 3b, blue circles). The reason is that away from resonance the optical constants are determined by the electron density, and the density of our $SrTiO_3$ substrate (5.12 g/cm^3) and the strained film (< 6 g/cm^3) do not differ significantly. Therefore from the x-rays' perspective the film/substrate ensemble looks like a semi-infinite layer, with reflectivity given by the Fresnel formulae.

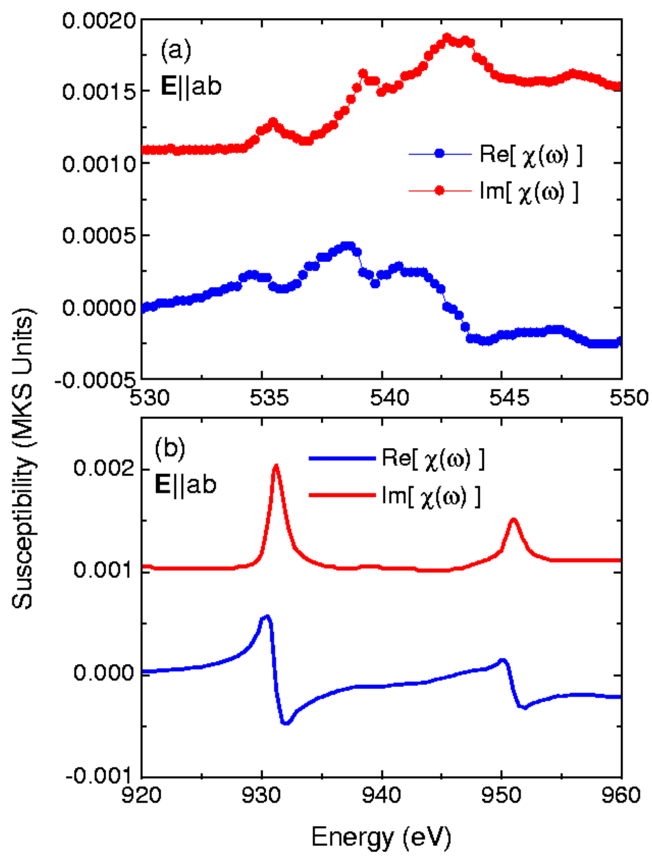

Figure 2. *ab plane susceptibility of optimally doped* $La_{2-x}Sr_xCuO_{4+\delta}$, *in MKS units, calculated by the procedure described, (a) in the vicinity of the Oxygen K edge and (b) the* $CuL_{2,3}$ *edge.*

If the energy is changed by only 2 eV to the mobile carrier peak, to point "B" in Fig. 1a, there is a 16% boost to the susceptibility of the film and beautiful fringes result (Fig. 3a, red circles). So the resonance provides the contrast needed to distinguish the film from the substrate.

The striking thing here is that the fringes in Fig. 3a come *only from the carriers* and are not related to the rest of the electrons in the film. If there were carrier ordering along the (001) direction this would be reflected as a modulation of the envelope of these fringes. Ordering *parallel* to the CuO_2 planes would result in the appearance of scattering in an off-specular geometry, i.e. in which the momentum transfer vector **q** has a component in the in-plane direction.

The enormity of the CuL effects are also demonstrable in this measurement. At the top of the Cu$L_{3/2}$ peak, interference fringes, which again are not visible off resonance, approach 10^6 photons/sec (Fig. 3b, green line). Reflectivity over the full angular range, off resonance as well as on the mobile carrier and CuL resonances, is shown in Fig. 3b.

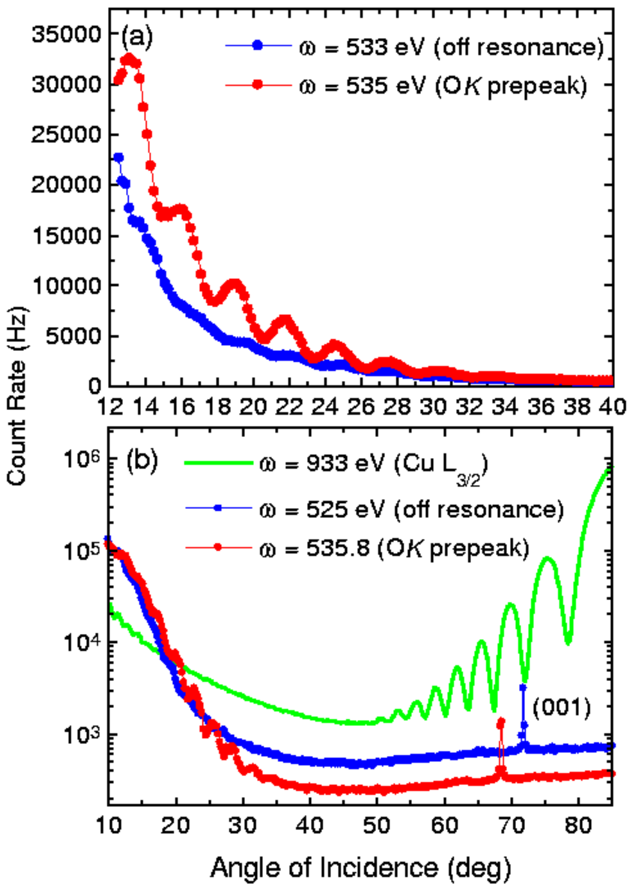

Figure 3. *Angle-dependent reflectivity of $La_2CuO_{4+\delta}$ (a) just below and on the mobile carrier peak at 535 eV, showing the resonant enhancement, and (b) over the full angular range for three different energies, 525 eV (far from resonance), 535.8 eV (on the mobile carrier peak), and 933 eV (on the Cu$L_{3/2}$ peak). Notice the (001) structural reflection at 70º Bragg angle.*

The careful observer will notice something strange. Because of the polarization dependence of our edge features and the fact that we are working with P polarized light one expects the interference fringes to grow toward higher scattering angles. This is because at high angles **E** lies parallel to the CuO_2 planes where the resonant enhancement is strongest. The CuL fringes at 933 eV do exactly that. The fringes at the mobile carrier peak do not. In fact, they *attenuate* at higher angles. Is this a sign of carrier inhomogeneity? Fluctuating stripes? Visons?

Maybe, but we will first offer a conservative explanation. In the most general sense what makes an object scatter light is spatial nonuniformity in its susceptibility. What makes a layer exhibit fringes is two localized discontinuities (the front and rear faces) that generate waves which beat against one another as the sample is rotated. The fringes will damp if one or both of these discontinuities is smeared over a depth larger than $\lambda/2$. Several things could potentially do this in our case: (1) a carrier depletion region due to the contact potential difference between the film and substrate, (2) oxygen interdiffusion at the substrate, or (3) structural reconstruction at the film-substrate interface induced by the polar nature of a (001) surface. Any of these phenomena can damp fringes by smoothing the discontinuity at the rear of the film.

The effect of smoothing can be easily demonstrated in the Born approximation, where the scattering amplitude is proportional to the Fourier transform of the susceptibility (Jackson, 1999). Since for a film the susceptibility varies in one dimension, as long as we consider only specular geometry (as in the current measurements) the scattering amplitude can be expressed in terms of one-dimensional integrals of the form

$$\chi(q) = \int_{-\infty}^{\infty} dx\, \chi(x)\, e^{iqx}$$

where $\chi(x)$ is the spatially-varying susceptibility and $q = 4\pi/\lambda \sin(\theta)$ is the momentum transfer. For an isotropic film of thickness L with susceptibility χ_F on a substrate with susceptibility χ_S this integral has the value

$$\chi(q) = \frac{\chi_F}{iq}\left(1 + e^{-iqL}\right) - \frac{\chi_S}{iq + \eta}$$

where a convergence factor $e^{i\eta x}$ has been added to attenuate the substrate at infinite distances. If the film is anisotropic the susceptibility is a tensor of the form

$$\chi(\mathbf{q}) = \begin{pmatrix} \chi_{ab}(q) & 0 \\ 0 & \chi_c(q) \end{pmatrix}$$

in which case the scattering matrix element, incorporating polarization effects, has the form

$$M = \epsilon_1 \cdot \chi(q) \cdot \epsilon_2$$

The simplest choice of parameters which is qualitatively consistent with our optical analysis, taking the substrate as a reference, is $\chi_S = 1$, $\chi_F^c = 1.03$, and $\chi_F^{ab} = 1.16$ at the prepeak and $\chi_F^{ab} = 1.78$ at the Cu$L_{3/2}$ peak. Plots of $|M|^2$ for both a sharp film profile and one that has been smoothed over 20 Å at the substrate are shown in Fig. 4. Notice that for a sharp layer the fringes at the carrier prepeak increase at high angles as expected. When the interface is smoothed they fade away. So the absence of fringe enhancement at high angles is at least consistent with a smoothing, though we cannot yet rule out other explanations.

In summary, we have demonstrated that through resonance effects the carriers in the cuprates can be enhanced in the x-ray scattering amplitude by a factor of 82. This is the first demonstration of a direct structural probe of the superconducting *ground state*. The spatial resolution of this technique is modest (λ/2 ~ 11 Å) but is adequate for exploration of many phenomena. The present work conspicuously omits the most important experiments: those with **q** parallel to the CuO_2 planes, which would be sensitive to in-plane ordering. Those measurements are forthcoming.

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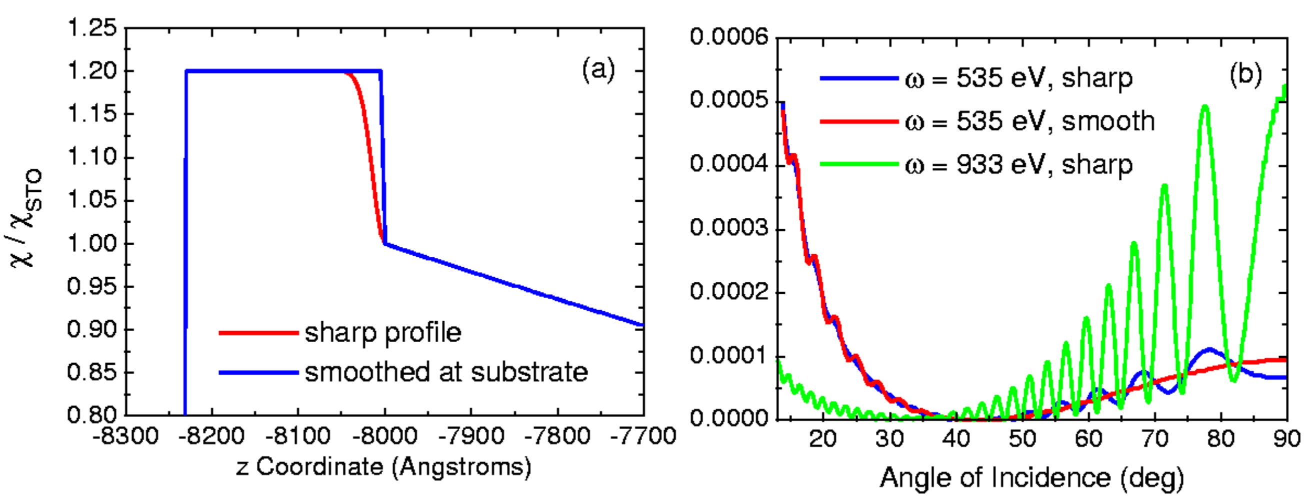

Figure 4. *(a) Susceptibility profiles representing (blue line) a perfect film on a substrate and (red line) the same smoothed to simulate a depletion layer, oxygen interdiffusion, or other effects. The sloping nature of the substrate (x > 8000 Å) is a numerical implementation of the convergence factor* $e^{i\eta x}$. *(b) Resulting interference fringes (relative units) for the two profiles, showing damping at high scattering angles for the smoothed layer.*

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